

Long Life Catalytic Membrane Reactors for Spontaneous Conversion of Natural Gas to Synthesis Gas

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Introduction

This program is focusing on the development of mixed ionic and electronic conducting materials based on the brownmillerite structure for use in catalytic membrane reactors (CMRs). These CMRs are being evaluated for promoting the spontaneous and highly selective oxidative reforming of carbon dioxide/natural gas mixtures to synthesis gas. The specific chemical reactions occurring within the CMR are:



A schematic illustration of the empirical processes occurring at the CMR surfaces during the combined methane partial oxidation/CO₂ reforming reactions is illustrated in Figure 1.

The production of synthesis gas from methane and higher hydrocarbons is currently performed by three basic processes: 1) steam reforming; 2) partial oxidation; and 3) autothermal reforming. In the first process, methane is reacted with steam to yield a synthesis gas of H₂:CO ratio >2. The disadvantages of this process are the endothermic nature of the steam reforming reaction and the high H₂:CO ratio which requires subsequent treatment if the synthesis gas is to be used for methanol or Fischer-Tropsch synthesis.

The drawback of the partial oxidation process is the requirement for oxygen. Oxygen adds costs both in terms of capital and operation. Although partial oxidation can be performed with air, this leads to a syngas product diluted with nitrogen. The advantage of partial oxidation is that it is exothermic. The third process, autothermal reforming, is a combination of the steam reforming and partial oxidation processes. It has the disadvantages of both of these processes. The selection of one of these processes is dependent upon the use of the syngas, the location and the economics of the overall process.

The drawbacks of the existing processes are overcome by performing the partial oxidation reaction within a CMR. First, the CMR serves to separate oxygen from the air. This results in a pure syngas product without the expense of producing oxygen. Second, because it is a partial

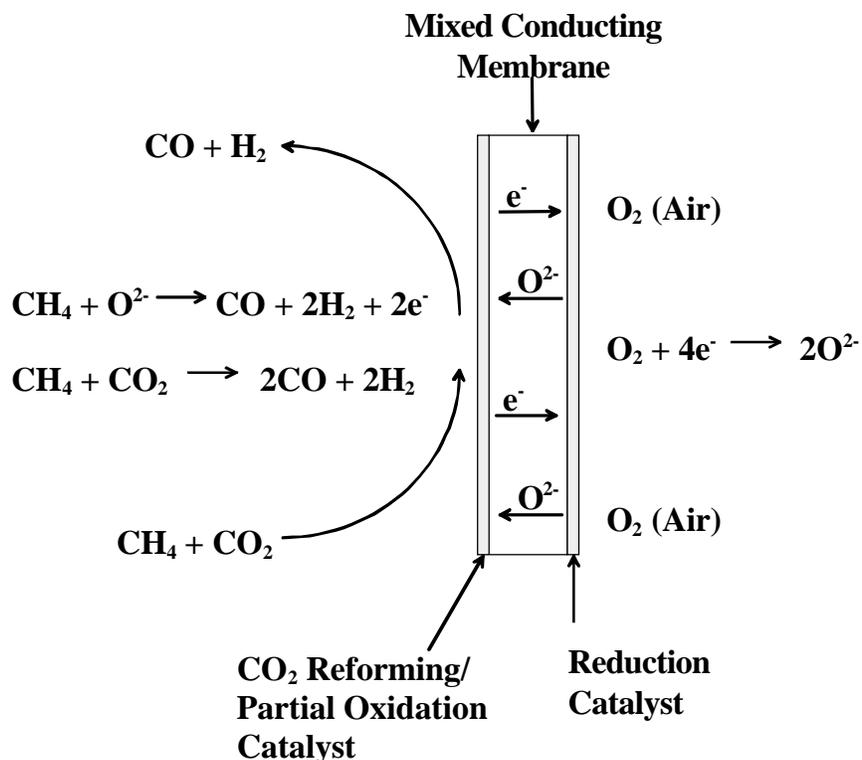


Figure 1. Schematic illustration of empirical processes occurring at the CMR surfaces during the combined partial oxidation/ CO_2 reforming reactions.

oxidation reaction, the overall reaction is still exothermic and no additional fuel is needed to drive the reaction.

A specific application of the CMR partial oxidation process is the conversion of remote natural gas. Remote natural gas is gas that cannot be economically brought to market. Because of the expected cost reductions associated with CMR technology relative to steam reforming or partial oxidation, the CMR process will be applicable to converting remote natural gas to syngas with subsequent conversion to liquid fuels such as methanol or diesel.

In addition to the CMR methane partial oxidation process, this project has also studied the combined methane partial oxidation/ CO_2 reforming processes. There are several advantages to the combined processes over the straight methane partial oxidation. The first is the CO_2 reforming process can be used as a method for thermal management within the CMR. As the partial oxidation process is exothermic, the heat generated must be removed from the reactor. This can be accomplished by using the endothermic CO_2 reforming process to absorb this heat. Figure 2 summarizes the thermodynamics of the combined processes and shows that there are ranges of temperature and concentration of CO_2 in the methane feedstock in which the combined processes are thermoneutral, *i.e.* $\Delta H=0$, and that net consumption of CO_2 occurs.

The second advantage of the combined processes is that methane and CO_2 are both greenhouse gases. This technology will therefore spontaneously convert two greenhouse gases into a valuable feedstock for subsequent conversion to liquid fuels such as methanol or diesel.

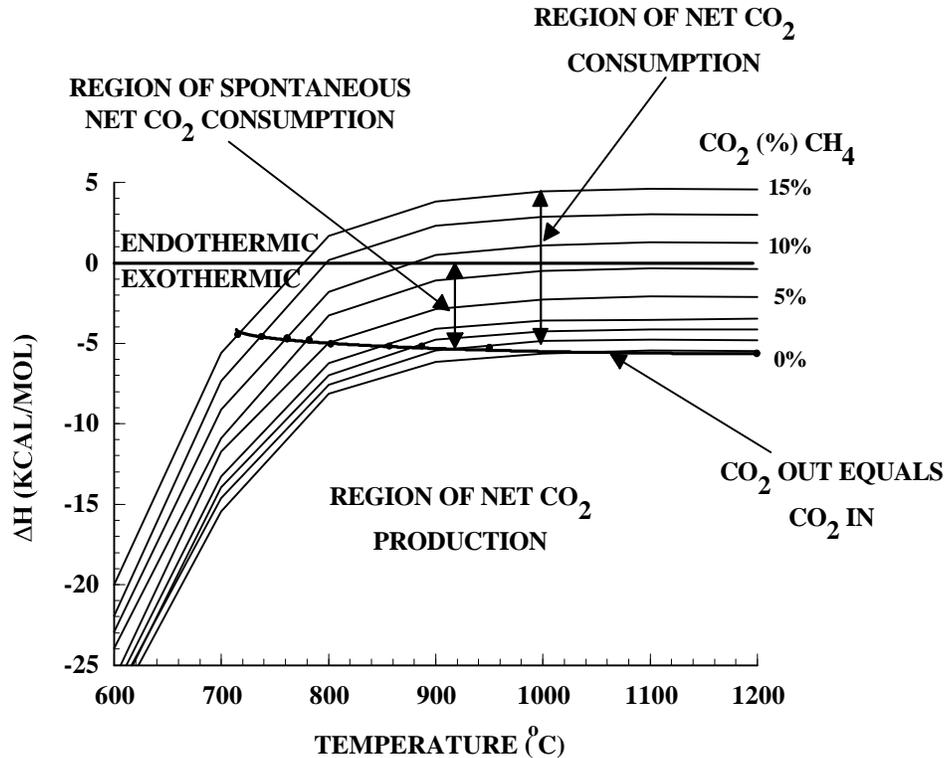


Figure 2. Plot of ΔH vs. temperature for the combined partial oxidation/ CO_2 reforming reactions as a function of the percentage of CO_2 in the feedstock.

Objectives

The objectives for this program are as follows:

- Synthesize and characterize mixed oxide ion and electron conductors based on the brownmillerite structure;
- Synthesize and characterize catalysts for promoting the combined partial oxidation/ CO_2 reforming processes;
- Prepare sintered disks, open-both-ends and closed-one-end tubes of the mixed conducting materials;
- Fabricate and evaluate disk and tube CMRs for the combined methane partial oxidation/ CO_2 reforming processes;
- Evaluate and optimize reactor design parameters for CMRs;
- Evaluate long-term performance of CMRs for the subject reactions.

Approach

The most important aspect of CMRs is the membrane material. Eltron has been studying ionic conductors¹ and mixed ionic and electronic conductors based on the brownmillerite structure. This structure has the general composition $A_2B_2O_5$ and is attractive as an oxide ion conductor since it can support a large population of oxide ion vacancies, both ordered and disordered, as well as a variety of substituents in the A and B lattice sites. The structure consists of BO_6 octahedral layers sharing vertices with a layer of BO_4 tetrahedra (Figure 3a). This difference in coordination sphere of B metal ions lends itself to controlled substitution. Depending on the particular metal ions, some distortion may be present in the polyhedra. This structure may be compared to the perovskite structure (Figure 3b) where B metal atoms occupy only octahedral sites with no inherent oxide ion vacancies. The brownmillerite structure can then be thought of as an ordered defect structure with defects due to oxygen vacancies associated with tetrahedral (octahedral in the perovskite structure) sites. The A metal ion coordination sphere varies but is typically nine or ten coordinate and distorted.

The rationale for selecting specific A and B lattice substituents within the $A_2B_2O_5$ brownmillerite structure has evolved in part from recent studies performed at Eltron¹⁻⁶ which have identified clear correlations between mixed conducting material crystallographic and thermodynamic parameters and the activation energy for ionic transport. These parameters include: 1) the average metal-oxygen bond energy within the mixed conductor, 2) lattice free volumes, obtained by subtracting the ionic volumes of cations and O^{2-} in the unit cell from the overall crystallographic unit cell, 3) the parameter r_{critical} (r_c) which corresponds to the radius of the opening between the two A site cations and one B site cation through which the mobile anion must pass, and 4) lattice polarizability towards ionic migration. Eltron is currently applying this rationale to the selection of new brownmillerite materials for use as mixed conducting membranes.

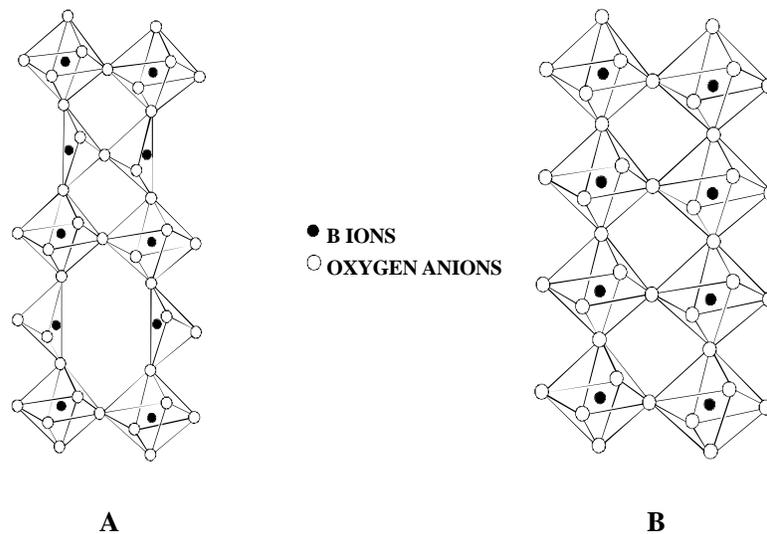


Figure 3. Comparison of brownmillerite (A) and perovskite (B) crystal structures.

Project Description

The current project is being addressed by:

- Selecting preferred brownmillerite mixed conducting membranes and surface catalysis for the carbon dioxide/natural gas oxidative reforming surface;
- Performing an in-depth study of catalytic membrane performance towards component optimization;
- Developing and optimizing fabrication techniques for tubular membrane reactors;
- Fabricating multi-tube catalytic membrane reactor stacks which will be subjected to extensive performance testing.

Results

One of the most important properties necessary for industrial use of this technology is long-term stability of the membrane materials under actual operating conditions. An example of the long-term stability of Eltron's brownmillerite-based membrane materials for methane partial oxidation is shown in Figure 4. In this experiment, a closed-one-end tube served as the membrane reactor. The tube had an inner diameter of 8.6mm with a wall thickness of 1.2mm. The exposed length was 3.5cm yielding an effective surface area of 9.5cm². The outside of the tube was coated with a partial oxidation catalyst consisting of Ni supported on a perovskite-type metal oxide. The inside of the tube was coated with La_{0.8}Sr_{0.2}CoO₃ which served as the oxygen reduction catalyst. The feed gas was 80% methane in helium and was passed over the outside of the tube. Air was used as the oxygen source and passed inside the tube. The experiment was performed at atmospheric pressure and 900°C.

As shown in Figure 4, the reactor has been operating for >5000hr with a syngas production rate between 10-15ml/min-cm² with a H₂:CO ratio that varied from 1.8 to 2, close to the expected value of 2. At ~700hr, there was a complete loss of activity because the methane tank serving the reactor ran empty. When the methane tank was replaced and the methane concentration returned to the previous value in the feed, the reactor resumed syngas production at a slightly lower, but steady rate. The reason for the lower production rate after restarting the reactor is not known but may be due to some loss of activity due to catalyst deactivation. No change in the H₂:CO ratio was observed after restarting the reactor. In addition to the syngas production, the CO₂ formed in the product was also monitored. The CO₂ produced was never more than 4% of the CO production rate indicating that no deep oxidation was occurring. During the course of this experiment, no evidence for mechanical or chemical instability was observed. Additionally, no leakage into the tube, as measured by the N₂ concentration in the product stream, was observed.

Further evidence of chemical stability is shown by x-ray diffraction (XRD) experiments performed on membrane materials operated in a methane partial oxidation CMR for extended time periods. For example, a reactor fabricated from a sintered disk was operated for >1000hr at

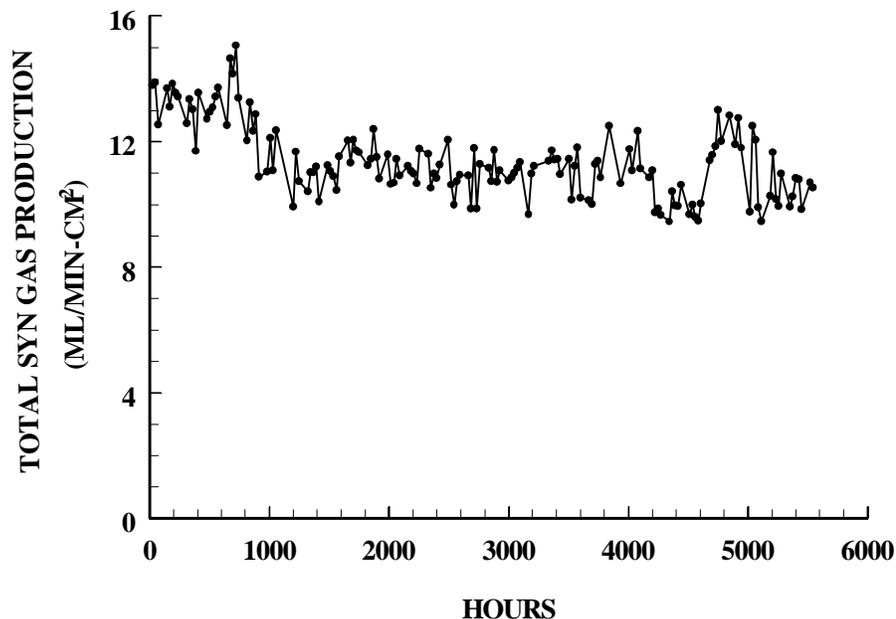


Figure 4. Plot of total syngas produced over time by the methane partial oxidation reaction within a brownmillerite based CMR.

900°C with a feed of ~80% CH₄ in helium. The oxygen partial pressure of the gas on the methane side of the membrane reactor was estimated to be 10^{-17} atm. After the reactor was voluntarily stopped, XRD was performed on the membrane partial oxidation surface. Figure 5 shows a comparison of this membrane surface with fresh powder. The two patterns are identical which indicates that even after this extended period of syngas production, the membrane material is stable with respect to chemical decomposition under operating conditions. Additionally, the membrane disk maintained its mechanical integrity over the course of the experiment.

Experiments on the combined methane partial oxidation/CO₂ reforming reactions within a CMR have also been performed. As a typical example, a sintered disk served as the membrane reactor. The effective surface area was 0.5cm² and the membrane thickness was 1.4mm. One side of the disk was coated with a partial oxidation/CO₂ reforming catalyst, specifically Rh (5wt%) supported on a metal oxide. The opposite side of the disk was coated with La_{0.8}Sr_{0.2}CoO₃ which served as the oxygen reduction catalyst. The feed gas consisted of 80% methane with CO₂ and helium making the balance. Air was used as the oxygen source and passed inside the tube. The experiment was performed at atmospheric pressure and 900°C.

Figures 6-8 summarize the results of this experiment. As shown in Figure 6, the amount of syngas produced initially increased and then decreased slightly with increasing CO₂ content in the feedstock. The H₂:CO ratio in the syngas product decreased as expected. Additionally, CO₂ was consumed in this process in the CMR. These results validate the concept of promoting the combined CH₄ partial oxidation/CO₂ reforming reactions within a brownmillerite-based CMR.

Application

As discussed previously, one of the driving forces for this technology is the expected economic benefits. We have performed an economic analysis of a CMR partial oxidation plant

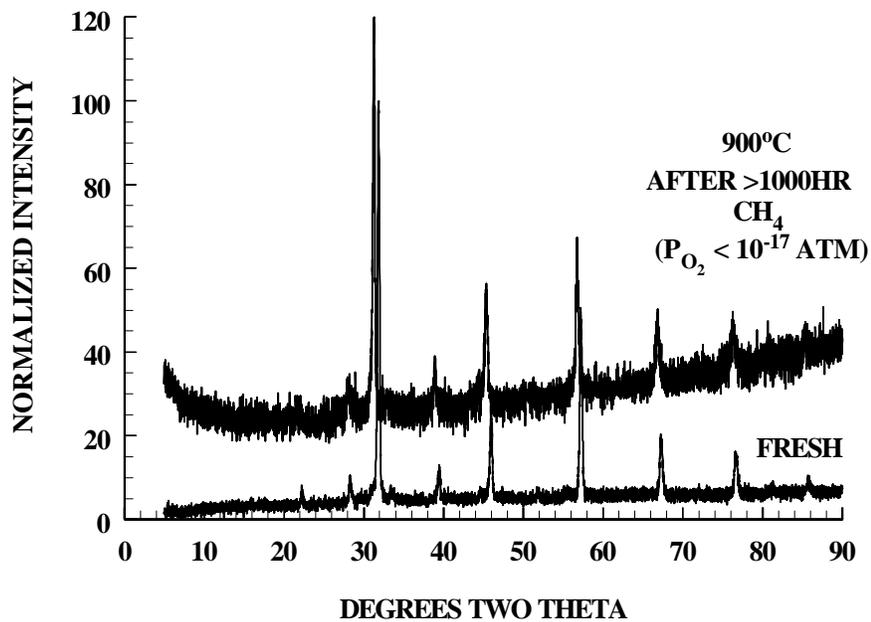


Figure 5. XRD patterns comparing as-prepared membrane material with that of the surface of a CMR exposed to methane during the methane partial oxidation process at 900 °C for >1000hr.

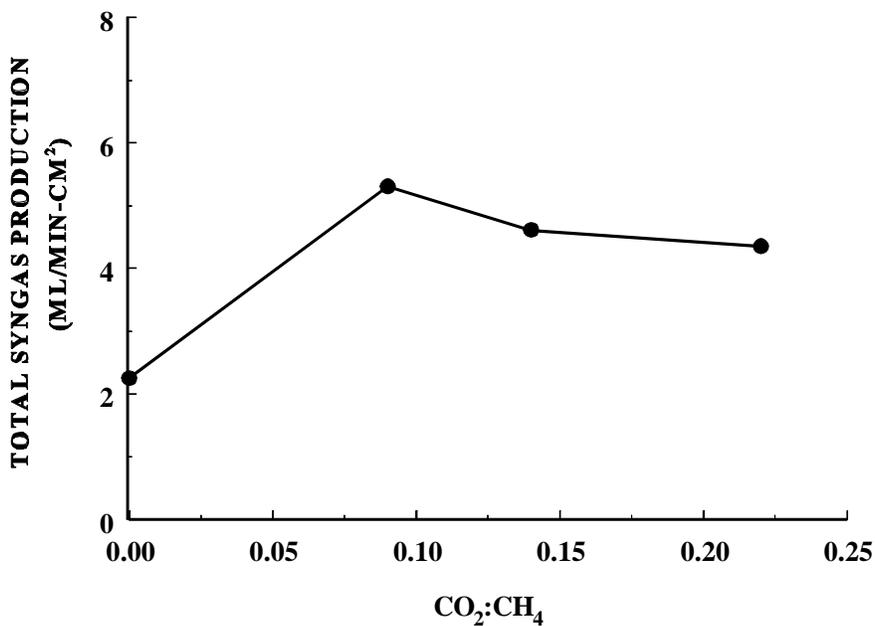


Figure 6. Plot of total syngas production as a function of the CO₂:CH₄ ratio in the feedstock for the combined methane partial oxidation/CO₂ reforming processes in a CMR at 900 °C.

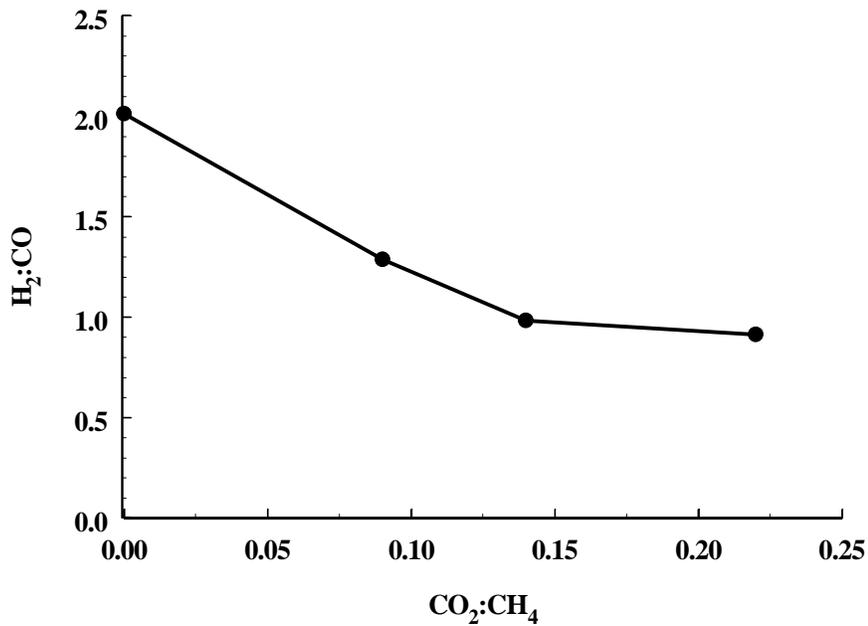


Figure 7. Plot of H₂:CO in the syngas product as a function of the CO₂:CH₄ ratio in the feedstock for the combined methane partial oxidation/CO₂ reforming processes in a CMR at 900 °C.

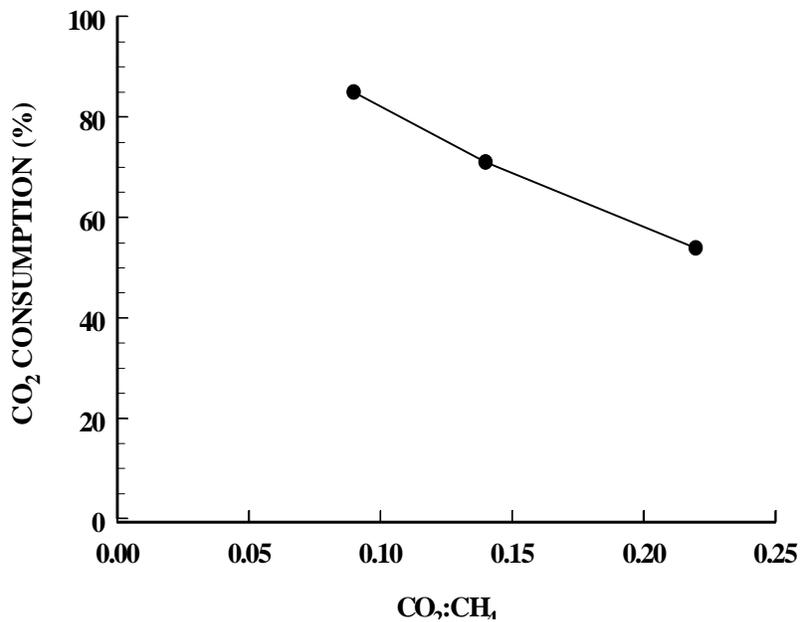


Figure 8. Plot of CO₂ consumption as a function of the CO₂:CH₄ ratio in the feedstock for the combined methane partial oxidation/CO₂ reforming processes in a CMR at 900 °C.

compared to a plant based on standard technology. In both cases, we have assumed that the syngas would be used to produce methanol at a scale of 25 million gallons per year. Table 1 summarizes these results. As can be seen in this Table, the Eltron CMR technology is expected to have a cost savings of 25-30%. As the historical price of methanol is 40-45¢, this is a very significant increase in profit margin. Most of the cost savings in the Eltron CMR process is obtained from lower capital costs as an oxygen plant is not required. Additionally, there are lower energy costs associated with the Eltron technology.

Future Work

Future work in this program will consist of the following:

- Optimization of process parameters such as flow rates, CO₂ concentrations in the feedstock, temperature, *etc.*;
- Optimization of catalyst compositions and supports;
- Evaluation of reactor configurations such as slurry-coated tubes, packed beds, turbulence promoters, *etc.*

Table 1.
Economic Comparison of Methanol Produced from Syngas Prepared from Standard Technology vs. Eltron CMR Technology

	<u>STANDARD TECHNOLOGY</u>	<u>ELTRON TECHNOLOGY</u>
Capital	\$25 Million	\$17 Million
9.5%, 15 Yr	\$3100K	\$1600K
Maintenance		
3.5% Capital	\$900K	\$600K
Energy	\$630K	\$0K
\$1.8MM/BTU		
Labor 4 Workers		
3 Shifts @ 50K	\$600K	\$600K
Feedstock		
\$1.8MM/BTU	<u>\$3800K</u>	<u>\$3800K</u>
	<u>36¢/Gal</u>	<u>26¢/Gal</u>

Acknowledgments

Eltron wishes to acknowledge the support of this work through the SBIR program of the U.S. Department of Energy under contract DE-FG02-94ER81748, 8/15/94-3/10/97, Rodney D. Malone, Project Officer.

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